A Self-Consistent Theory for the Inter- and Intramolecular Correlation Functions of a Hard-Sphere-Yukawa-Chain Fluids *

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An extended test-particle method is used to predict the inter- and intramolecular correlation functions of freely jointed hard-sphere-Yukawa-chain fluids by calculating the segmental density distributions around a fixed segment. The underlying density functional theory for chain fluids is based on a modified fundamental measure theory for the hard-sphere repulsive and a mean-field approximation for attraction between different segments. The calculated intra- and inter-molecular distribution functions agree well with the results from Monte Carlo simulations, better than those from alternative approaches.

The conventional method for investigating the microscopic structures of uniform polymeric fluids is the polymer integral equation theory.[1] However, to solve the intermolecular total and direct correlation functions from the polymer integral equation theory, the intramolecular correlation functions are typically unknown and must be assumed in advance using a simplified model or calculated by Monte Carlo simulations. An alternative approach has been recently proposed by Stell and co-workers.[2,3] based on the product-reactant Ornstein–Zernike equation, Wertheim's thermodynamic perturbation theory and polymer Percus–Yevick closure. While this new approach provides both inter- and intra-molecular correlation functions, it incorrectly predicts that the intramolecular correlation function is independent of density and temperature. A self-consistent theory for both inter- and intra-molecular correlation functions of polymeric fluids is yet to be developed.

As proposed long ago by Percus,[4] the radial distribution function of a uniform fluid can be represented by the local inhomogeneity of density distributions around an imaginarily fixed particle. Such density distributions can be calculated using a density functional theory.[5,6] In a previous work[7] we have extended Percus' idea for polymeric systems and used it to investigate the inter- and intramolecular correlation functions of hard-sphere-chain fluids. In this Letter, we utilize a similar approach to investigate the microscopic structures of polymers with attractive force represented by the Yukawa potential.

We consider freely jointed chain fluids where the site–site potential between any pair of beads i and j is represented by the attractive Yukawa potential

$$u_{ij}(r) = \begin{cases} \infty, & r < \sigma, \\ -\varepsilon e^{-z(r-\sigma)/\sigma}/(r/\sigma), & r > \sigma, \end{cases} \quad (1)$$

where σ is the hard-sphere diameter, ε is the potential

well depth, and $z = 1.8$ is fixed in this work. For convenience, we use the dimensionless quantities throughout this work: $T^* = kT/\varepsilon$ and $\eta = \pi\rho\sigma^3 M/6$, where k is the Boltzmann constant, T is the temperature, ρ is the number density of the chain molecules, and M is the chain length. The above model has proven to be a good approximation for alkanes.[8]
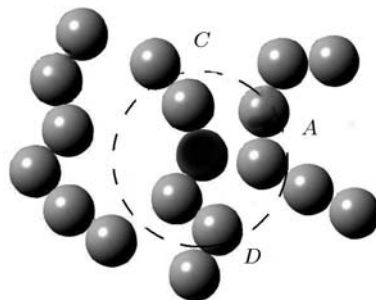

Fig. 1. Extended Percus trick.

Following our previous work,[7] one chain molecule, designed as B consisting of C and D, is tethered by placing a segment at the origin (see Fig. 1). All other molecules, designated as A, are freely distributed around the central chain. The two flying fragments of chain B are further labelled as C and D, respectively. At equilibrium, the density profiles of free chains and the tethered fragments satisfy the variational relations

$$\frac{\delta\Omega}{\delta\rho^{(A)}(\boldsymbol{R}^{(A)})} = \frac{\delta\Omega}{\delta\rho^{(C)}(\boldsymbol{R}^{(C)})} = \frac{\delta\Omega}{\delta\rho^{(D)}(\boldsymbol{R}^{(D)})} = 0, \quad (2)$$

where Ω is the grand potential functional, $\rho^{(l)}(\boldsymbol{R}^{(l)})$ ($l = A, C, D$) represents the density profile for the chain l, and $\boldsymbol{R}^{(l)} = \{\boldsymbol{r}_1^{(l)}, \boldsymbol{r}_2^{(l)}, \ldots, \boldsymbol{r}_{M_l}^{(l)}\}$ represents a composite vector that specifies the positions of M_l segments of chain l. The segmental distributions of the

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free molecules around the fixed segment is related to the intermolecular radial distribution functions

$$g(r) = \frac{1}{M_A^2} \sum_{i=1}^{M_A} \sum_{j=1}^{M_A} g_{ij}(r)$$

$$= \frac{1}{M_A^2} \sum_{i=1}^{M_A} \sum_{j=1}^{M_A} \rho_{si,j}^{(A)}(r)/\rho_b, \qquad (3)$$

where $\rho_{si,j}^{(A)}(r)$ is the density profile of segment i on the free molecules around the fixed segment j, and ρ_b is the bulk segmental density. The distributions of the segments in the fragments C and D are directly related to the average intramolecular correlation functions $w(r)$,

$$w(r) = \frac{1}{M_A} \sum_{i=1}^{M_A} \sum_{j=1}^{M_A} w_{ij}(r) = \frac{1}{M_A} \sum_{i=1}^{M_A} \sum_{j=1}^{M_A} \rho_{si,j}^{(B)}(r). \qquad (4)$$

Because there is only one tethered chain, the segmental densities of chain B satisfy the normalization condition

$$\int \rho_{si,j}^{(B)}(r)d\boldsymbol{r} = 1. \qquad (5)$$

Once we have an expression for the grand potential, the density profiles of free and tethered segments can be determined by Eq. (2). In this Letter, such an expression is derived from an extension of the density functional theory developed by Yu and Wu[7] by including the van der Waals potential (Yukawa potential) through mean-field approximation.[9] The system considered above is equivalent to a mixture of three polymeric components $(A + C + D)$ in a spherically symmetric external field due to the fixed segment. The grand potential functional Ω is related to the Helmholtz energy functional F via a Legendre transform

$$\Omega = F[\rho^{(A)}(\boldsymbol{R}^{(A)}), \rho^{(C)}(\boldsymbol{R}^{(C)}), \rho^{(D)}(\boldsymbol{R}^{(D)})]$$

$$+ \sum_{l=A,C,D} \int [\Psi^{(l)}(\boldsymbol{R}^{(l)}) - \mu_l]\rho^{(l)}(\boldsymbol{R}^{(l)})d\boldsymbol{R}^{(l)}, \qquad (6)$$

where $d\boldsymbol{R}^{(l)} = d\boldsymbol{r}_1^{(l)} d\boldsymbol{r}_2^{(1)} \ldots d\boldsymbol{r}_{M_l}^{(l)}$ represents a set of differential volumes for the polymer chain l of M_l segments, μ_l is the chemical potential of chain l, and $\Psi^{(l)}(\boldsymbol{R}^{(l)})$ denotes the total external potential on chain l. The total external potential acting on each molecule is equal to the sum of the potential energy on its individual segments $\Psi^{(l)}(\boldsymbol{R}^{(l)}) = \sum_{i=1}^{M_l} \varphi_i^{(l)}(\boldsymbol{r}_i^{(l)})$.

The ideal gas contribution to the Helmholtz energy functional is exactly known.[10] The excess Helmholtz energy functional F_{ex} is decomposed into contributions due to the non-bonded hard-sphere repulsion and van der Waals attractions as well as chain connectivity:

$$F_{ex} = kT \int d\boldsymbol{r}[\Phi^{\text{hs}} + \Phi^{\text{chain}}] + \int d\boldsymbol{r} f_{\text{ex}}^{\text{att}}(\boldsymbol{r}), \qquad (7)$$

where Φ^{hs} and Φ^{chain} are, respectively, the reduced excess Helmholtz energy densities due to hard sphere repulsion[5] and chain connectivity.[7,10] They can be obtained from the modified fundamental measure theories for hard-sphere fluids and polymers, respectively. The modified approximation applied to the attractive part of the site-site interaction potential is[9]

$$f_{\text{ex}}^{\text{att}}(\boldsymbol{r}) = \frac{1}{2} \int d\boldsymbol{r}'\rho(\boldsymbol{r})\rho(\boldsymbol{r}')u_{\text{att}}(|\boldsymbol{r} - \boldsymbol{r}'|). \qquad (8)$$

Minimization of the grand potential with respect to the density profiles of free and tethered chains yields the average segmental density

$$\rho^{(l)}(\boldsymbol{r}) = \exp(\beta\mu_l) \int d\boldsymbol{R}^{(l)} \sum_{i=1}^{M_l} \delta(\boldsymbol{r} - \boldsymbol{r}_i^{(l)})$$

$$\cdot \exp[-\beta V_b^{(l)}(\boldsymbol{R}^{(l)}) - \beta \sum_{j=1}^{M_l} \lambda_j^{(l)}(\boldsymbol{r}_j^{(l)})], \qquad (9)$$

where $l = A, C$ and D, and $V_b^{(l)}(\boldsymbol{R}^{(l)})$ is the total bonding potential for a chain l, i.e.

$$V_b^{(l)}(\boldsymbol{R}^{(l)}) = -kT \sum_{i=1}^{M_l-1} \ln\left[\frac{\delta(|\boldsymbol{r}_i - \boldsymbol{r}_{i+1}| - \sigma)}{4\pi\sigma^2}\right] \qquad (10)$$

and $\lambda_j^{(l)}(\boldsymbol{r}_j^{(l)})$ is related to the excess Helmholtz energy functional F_{ex} and the external potential $\varphi_j^{(l)}(\boldsymbol{r}_j^{(l)})$ by

$$\lambda_j^{(l)}(\boldsymbol{r}_j^{(l)}) = \frac{\delta F_{\text{ex}}}{\delta \rho^{(l)}(\boldsymbol{r}_j^{(l)})} + \varphi_j^{(l)}(\boldsymbol{r}_j^{(l)}). \qquad (11)$$

Due to the spherical symmetry, the density profiles of both free and tethered segments vary only in the radial direction, i.e.

$$\rho^{(l)}(\boldsymbol{r}) = \rho^{(l)}(r). \qquad (12)$$

Substituting Eq. (10) into Eq. (9) and after some algebra simplification, we obtain the density profile of segments

$$\rho_{si}^{(l)}(r) = \exp(\beta\mu_l) \exp[-\beta\lambda_i^{(l)}(r)]G_L^{(l)i}(r)G_R^{(l)i}(r), \qquad (13)$$

where $G_L^{(A)i}(r)$ is the Green function for $l = A$ (free molecule), which is determined from the recurrence relation

$$G_L^{(A)i}(r) = \int dr' \exp[-\beta\lambda_i^{(A)}(r')]$$

$$\cdot \frac{r'\theta(\sigma - |r' - r|)}{2\sigma r}G_L^{(A)i-1}(r') \qquad (14)$$

for $i = 2, \ldots, M_A$ with $G_L^{(A)1}(r) = 1$. For a free chain A, we have the additional symmetric relation

$$G_R^{(A)M-i+1} = G_L^{(A)i}. \qquad (15)$$

For $l = C$ and D, the density distributions of the two immediate neighbours of the fixed segment are obtained by

$$\rho_{s1}^{(C)}(r) = \rho_{s1}^{(D)} = \delta(r - \sigma)/4\pi\sigma^2. \qquad (16)$$

The Green function for the next immediate neighbours is determined by

$$G_L^{(l)2} = \exp[-\beta\lambda_2^{(l)}(\sigma)]\frac{\theta(\sigma - |r - \sigma|)}{2r} \qquad (17)$$

and those for the remaining segments are calculated by iteration

$$G_L^{(l)i}(r) = \int dr' \exp[-\beta\lambda_i^{(l)}(r')]$$
$$\cdot \frac{r'\theta(\sigma - |r' - r|)}{2\sigma r}G_L^{(l)i-1}(r') \qquad (18)$$

for $i = 3, \ldots, M_l$ and $l = C, D$. The function $G_R^{(l)i}(r)$ is obtained from

$$G_R^{(l)i}(r) = \int dr' \exp[-\beta\lambda_i^{(l)}(r')]$$
$$\cdot \frac{r\theta(\sigma - |r' - r|)}{2\sigma r'}G_R^{(l)i+1}(r') \qquad (19)$$

with $G_R^{(l)M_l}(r) = 1$.

The chemical potential for free chains A is obtained from Wertheim's first-order thermodynamic perturbation theory:[11]

$$\beta\mu_A = \ln\rho_A + \beta\mu_A^{\rm hsc} - 4\pi\rho_b\sigma^3\frac{M_A}{T^*}\frac{1 + z}{z^2}, \qquad (20)$$

where $\rho_b = M_A\rho_A$ is the bulk density of segments, $\mu_A^{\rm hsc}$ is the excess chemical potential of corresponding hard sphere chain fluid.[11] The chemical potentials of the fragments C and D are determined by the normalization conditions, i.e. Eq. (5).
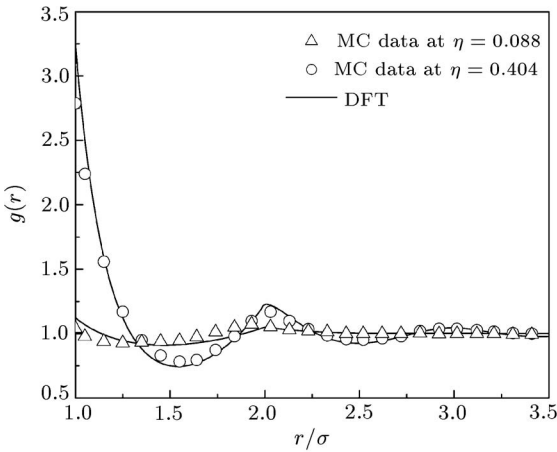

Fig. 2. Average radial distribution functions of Yukawa at $T^* = 2.8$ and $\eta = 0.088$ and 0.404, representing low and high densities. The simulation data are from Kalyuzhnyi *et al.*[12]

Here we calculate the inter- and intra-molecular radial distribution functions of freely jointed Yukawa fluids with chain length $M = 2, 4$ and 8. In the calculation, we fix the segments of a Yukawa chain one by one and calculate the density profiles around the fixed segment with Eqs. (13)–(20). Because of the symmetry, only $M/2$ calculations are required for predicting the

average radial distribution functions. In Figs. 2 and 3, the predicted average radial distribution functions are compared with the corresponding Monte Carlo simulation data[12] for the Yukawa at reduced temperatures $T^* = 2.8$ and 5.0, respectively. Good agreement is achieved for Yukawa at all the values of the reduce temperature T^* and packing fraction η studied, except for distances in the vicinity of contact where the theory overestimates the radial distribution functions.
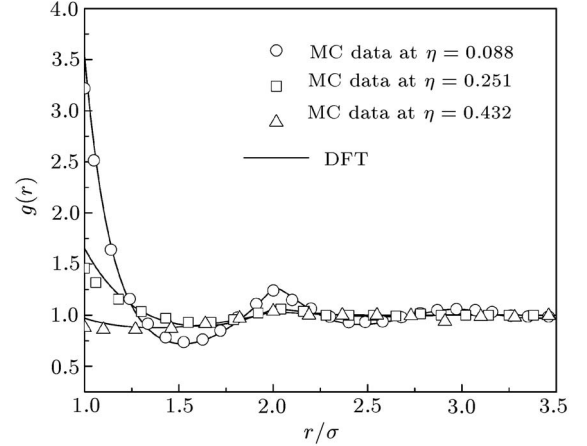

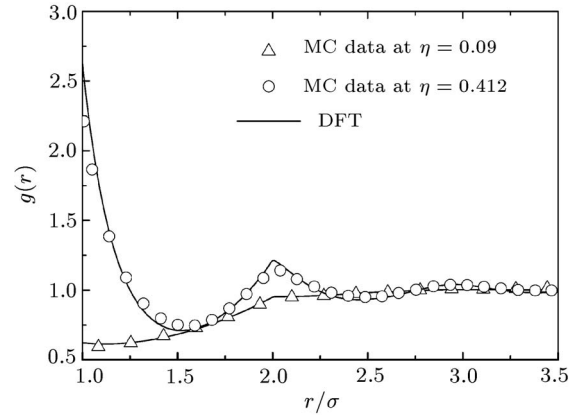**Fig. 3.** The same as Fig. 2 but $T^* = 5.0$ and $\eta = 0.088$, 0.251 and 0.432.

Fig. 4. Average intermolecular radial distribution functions of the hard-sphere-Yukawa 4-mers at $T^* = 5.0$ and $\eta = 0.09$ and 0.412.

Figures 4 and 5 present the average intermolecular radial distribution functions for the hard-sphere-Yukawa 4-mers and 8-mers, respectively. The depletion of the intermolecular segments at low density is due to the chain connectivity and van der Waals attraction, while the opposite trend at high density is due to the packing effect. From Figs. 4 and 5 we can see that the predictions from the present method are in good agreement with the simulation results[12] at both low and high densities. For comparison, the theoretical predictions from the polymer mean spherical approximation (PMSA) version[12] of the product-reactant Ornstein–Zernike approach[13] are also shown

in Fig. 5. In contrast to the present method, the PMSA theory overestimates the average intermolecular radial distribution functions for Yukawa 8-mers at low density ($\eta = 0.085$). At high density, the present method also provides slightly more accurate intermolecular radial distribution functions.
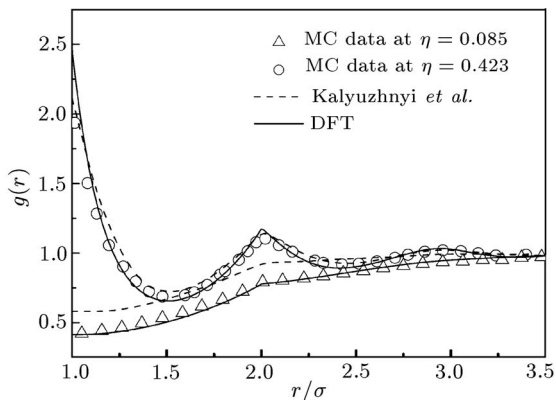

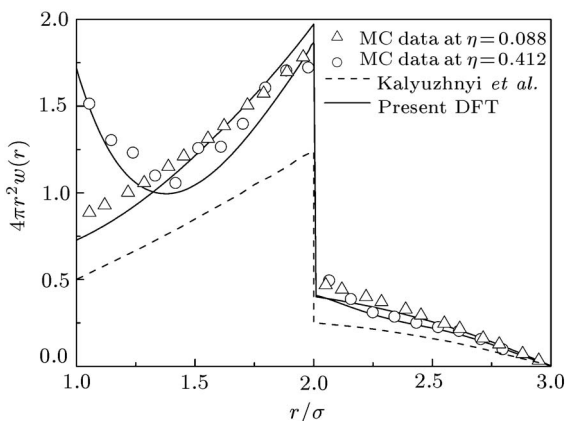**Fig. 5.** The same as Fig. 4 but for 8-mers at $T^* = 5.0$ and $\eta = 0.085$ and 0.423.

Fig. 6. Average intramolecular correlation functions of the hard-sphere-Yukawa 4-mers at $T^* = 5.0$ and $\eta = 0.088$ and 0.412. The simulation data are from Kalyuzhnyi *et al.*[12]

In Figs. 6 and 7, we compare the predictions of the average nonbonded intramolecular correlation functions $4\pi r^2 w(r)$ with corresponding Monte Carlo simulation results by Kalyuzhnyi *et al.*[12] for the hard-sphere-Yukawa 4-mers and 8-mers, respectively. Also shown in these figures are the predictions from the PMSA theory of Kalyuzhnyi *et al.*[12] The discontinuity at $r = 2\sigma$ is due to the direct interaction between next nearest neighbours along the polymer chain. For $r < 2\sigma$, the intramolecular radial distribution function increases monotonically with separation at low density. However, as the density increases it shows a minimum at approximate $r = 1.5\sigma$. For $r > 2\sigma$, the intramolecular correlation functions show the features of nonmonotonic decay. One can see from Figs. 6 and 7 that the intramolecular correlation functions from the PMSA theory of Kalyuzhnyi *et al*[12] are only

in qualitative agreement with the Monte Carlo simulation data, and are independent of the density of Yukawa chain fluid. The intramolecular radial distribution functions predicted from the present method improves significantly. Similar to the case for hard-sphere-chain fluids, the agreement between the present method and simulation is only semi-quantitative, especially in the vicinity of contact. This discrepancy is likely related to the approximation in representing the excess Helmholtz energy functional due to the chain connectivity.
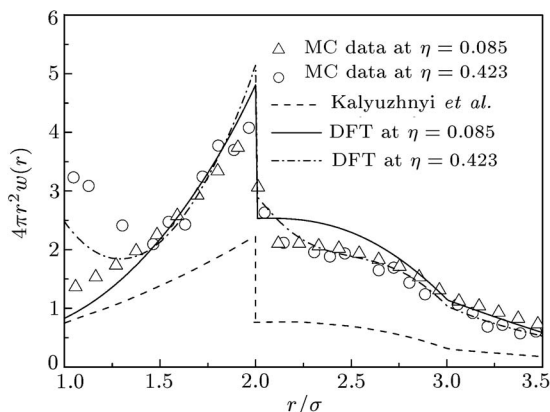

Fig. 7. The same as Fig. 6 but for 8-mers at $T^* = 5.0$ and $\eta = 0.085$ and 0.423.

In conclusion, we have used the extended test-particle method to predict both inter- and intra-molecular correlation functions of freely jointed hard-sphere-Yukawa-chain fluids. The density functional theory used in the calculation of the segmental density profiles is an extension of that by Yu and Wu,[7,10] where the Helmholtz energy functional due to the attractive potential is included by the mean-field approximation. The present method predicts intra- and inter-molecular correlation functions in good agreement with the simulation results. In comparison with alternative approaches in the literature, the present method has the advantage of predicting the nonideal behaviour of both inter- and intra-molecular correlation functions self-consistently.

References

[1] Chandler D et al 1972 *J. Chem. Phys.* **57** 1930
[2] Lin C T et al 1998 *J. Chem. Phys.* **108** 6513
[3] Stell G et al 1999 *J. Chem. Phys.* **110** 5444
[4] Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* (San Diego, CA: Academic)
[5] Yu Y X et al 2004 *J. Chem. Phys.* **121** 1535
[6] Li W H et al 2003 *Chin. Phys. Lett.* **20** 259
[7] Yu Y X and Wu J Z 2003 *J. Chem. Phys.* **118** 3835
[8] Fu D, Li Y-G and Lu J-F 2004 *Acta Chim. Sin.* **62** 1034
[9] Henderson D 1992 *Fundamentals of Inhomogeneous Fluid* (New York: Dekker)
[10] Yu Y-X and Wu J Z 2002 *J. Chem. Phys.* **117** 2368
[11] Chapman W G et al 1988 *Mol. Phys.* **65** 1057
[12] Kalyuzhnyi Y V et al 2002 *Mol. Phys.* **100** 2499
[13] Kalyuzhnyi Y V et al 1998 *J. Chem. Phys.* **108** 6525